

THEORETICAL INVESTIGATION OF H₂ COMBUSTION ON α -Al₂O₃ SUPPORT

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ABSTRACT

Based on Density Functional Theory – Generalized Gradient Approximation calculations (DFT-GGA), we provide a theoretical model for the effect of the catalytic support (α -Al₂O₃) on the dissociation of H₂, O₂, OH, H₂O, and the surface diffusion of oxygen and hydrogen species along the α -Al₂O₃ (0001) surface. These processes are key to understanding the ‘inverse spillover effect’ that occurs during hydrogen combustion on alumina surfaces. Our results indicate the dissociation of O₂ is not thermodynamically favored on the α -Al₂O₃ surface. However, both H₂ and H₂O can dissociate, forming hydroxyls with oxygen atoms in the second atomic layer. Once dissociated, oxygen species can diffuse locally but encounter a large barrier to long-range surface diffusion in the absence of defects or other species. In contrast, the barrier to the long-range surface diffusion of hydrogen is modest under ideal conditions.

1. INTRODUCTION

As the electronics behind the future warrior systems become more sophisticated, the weight of the batteries is an ever-increasing burden. One solution is to create a compact micro-burner device as shown in Figure 1 (Norton et al., 2004) that combusts a higher energy density fuel such as methane (energy density = 3053 W-hr/kg compared to 125 W-hr/kg for Li-ion batteries) and converts the released enthalpy into electrical power.

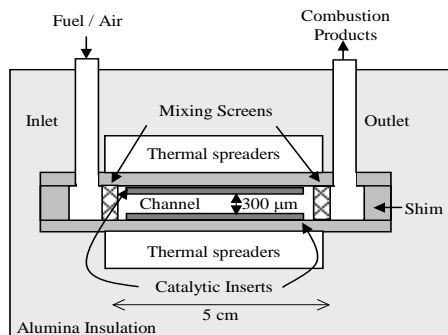


Figure 1: Microburner Schematic; Note: catalytic insert consists of nanosized Pt dispersed within porous Al₂O₃

Although there are many computational studies that detail the complete H₂ combustion mechanism for reactant and product species interacting with the catalytically active Pt cluster (Mhadeshware and Vlachos, 2007), few studies consider the effect of the Al₂O₃ support. New reaction pathways can arise due to support surface termination and reactivity at the Al₂O₃/Pt interface. One example of such a pathway is the “inverse spillover effect” (ISE) which occurs when H₂O chemisorbs or dissociates on the support forming mobile species that can migrate to the catalytically active particle and further promote combustion. Experimental evidence for ISE comes from the work of Wang et al. 1996 who demonstrated that CO can liberate H₂ from H₂O bound to Al₂O₃ support. In this paper, we seek to augment the current model for H₂ micro-combustion to include reactions that are initiated on the catalytic support. Specifically, we propose a mechanism by which H₂O and H₂ dissociate on the support forming hydroxyl groups which can further dissociate and diffuse to the catalytic particle.

2. MODEL PARAMETERS AND VALIDATION

2.1 α -Al₂O₃ Surface Termination

Our model (see Figure 2) consisted of a nine atomic layer thick Al terminated (0001) slab that is repeated under periodic boundary conditions as a 2x2 supercell with P1 symmetry and a 30 Å vacuum layer to prevent any interaction between periodic images. We chose this surface based on the availability of experimental and theoretical data in the literature as well as the work of Marmier et al., 2004 who calculated surface phase diagrams as a function of temperature and the O and H partial pressures for several different crystal orientations and surface terminations. The lattice parameters for the rhombohedral unit cell ($a=b=4.749$ Å, $c=12.991$ Å) were taken directly from experimental results (Swansen, 1960) and were not optimized during the simulation. In addition, we constrained the bottom two layers of the slab to reflect the bulk Al₂O₃ geometry.

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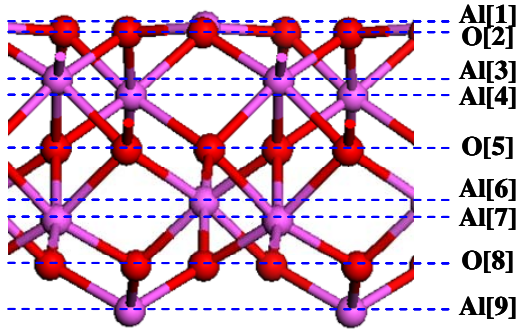


Figure 2: Cross section of fully relaxed Al terminated $\alpha\text{Al}_2\text{O}_3$ (0001) slab used for calculation. Oxygen and aluminum atoms are red and magenta respectively.

2.2 Model Parameters

All calculations were performed using ideal conditions (0 K, ultra high vacuum, defect free surface). The calculations were executed within the DMol³ (Delley, 2000) module of the Materials Studio (version 4) software package using a double-numeric basis set with polarization functions (DNP) and the Perdew-Burke-Ernzerhof (PBE- Perdue, 1996) version of the generalized gradient approximation (GGA-) to represent the electron exchange and correlations. The ion cores were described by a density functional semi-core pseudopotential (DSPP-Delley, 2002).

To validate our calculations, we compare our results for the surface reconstruction of the relaxed $\alpha\text{Al}_2\text{O}_3$ (0001) slab with the results of other theoretical and experimental investigations (see Table 1). In agreement with other theoretical studies, our simulation predicts an 89% contraction of the inter-atomic spacing of top surface layer and 6% expansion of the first sub-layer for the ultra-clean $\alpha\text{Al}_2\text{O}_3$ (0001) surface. The predicted surface reconstruction was explained by Sousa et al. 1993 as a

result of charge redistribution due to the highly ionic nature of alumina. The experimental value for this relaxation is closer to ~50%. The discrepancy between theoretical prediction and experimental measurements may be due to the difficulty in preparing a perfectly terminated surface with no adsorbed atoms or defects.

To simulate adsorption phenomena, we added one adsorbate molecule per supercell which is equivalent to approximately 1/12 monolayer according to Verdozzi et al. 1999 who define a monolayer as having one metal atom per surface oxygen. Binding energies were computed by subtracting the energy of the clean fully relaxed slab and the adsorbent molecule (H_2O , O_2 , H_2) from the total energy of the system after adsorption. We performed barrier calculations using the linear synchronous transit (LST) method of Govind et al, 2003 to extrapolate between reactant and product structures along the diffusion pathways illustrated in Figure 3.

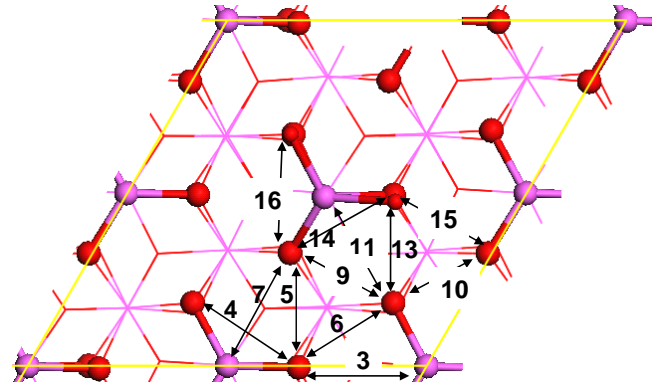


Figure 3: Top view of a 2x2 supercell showing allowed surface binding sites. The numbers correlate with the dissociation product and diffusion path notation referred to throughout the paper. When referring to dissociation products, the endpoints of the line indicate the atoms to which the dissociated species bind.

Table 1: Comparison of Theoretical and Experimentally Measured Changes in the Inter-atomic Layer Spacing of Al Terminated $\alpha\text{Al}_2\text{O}_3$ (0001) Slab with respect to their Unrelaxed Geometry

	Theoretical							Experimental	
	Ours	Hinneman	Verdozzi	Hass	Alavi	Ruberto	Carrasco	Guenard	Ahn
#Oxygen layers	3	9	18	3	3	9	11		
Functional	PBE/DSPP	PBE/PAW	LDA/NCPP	PBE/NCPP	PW91/USPP	PW91/NCPP	PBE/PAW		
Al ^[1] -O ^[2]	-89.2	-86.4	-87.4	-98	-97	-85.5	-93.8	-51	63
O ^[2] -Al ^[3]	+6	+4	+3.1	+5	+2	+3.2	+6.1	+16	
Al ^[3] -Al ^[4]	-39.9	-45.4	-41.7	-48	-53	-45.4	-46.7	-29	
Al ^[4] -O ^[5]	+18.9	+20.5	+18.3	+21	-27	+19.8	+22.0	+20	
O ^[5] -Al ^[6]	+17.1	+5	+5.6			+4.8	+8.5		
Al ^[6] -Al ^[7]	-31.2	-6.8	-8.3			-7.1	-11.6		
Al ^[7] -O ^[8]	0	+1.3	+1.1			+1.3	+2.2		
O ^[8] -Al ^[9]	0	-1.3	-0.5			-0.8	+0.7		
Al ^[9] -Al ^[10]		+4.6	+6.4			+3.0	+3.8		
Al ^[10] -O ^[11]		-1.2	-0.6			-0.7	-3.2		

2.3 Electron Spin State

The reaction chemistry of oxygen involved reactions on Al_2O_3 surfaces cannot be adequately described without careful consideration of the triplet- to-singlet spin conversion that occurs when the $2p/1s^*$ orbitals hybridize with the surface states. We find the energy difference between the triplet and the singlet ground state of free O_2 to be 19.3 kcal/mol which is in good agreement with the experimentally measured value of 22.6 kcal/mol (Herzberg, 1950). Figure 4 shows adsorption structures and dissociation products for O, H, O_2 , H_2 , and H_2O on the Al terminated - $\alpha\text{Al}_2\text{O}_3$ (0001) surface. For all adsorption / dissociation products except Figure 4A, 4E, and 4J, the lowest energy spin state was singlet. In Table 2, we detail the key molecular features for these structures as well as their binding energies. From Table 2, it is clear that triplet states result in tighter O=O bonds and a local elongation of the $\text{Al}^{[1]}-\text{O}$ bonding scheme. The spin state has no apparent effect on the length of hydroxyl or $\text{Al}^{[1]}-\text{H}^{[\text{ads}]}$ bonds. The triplet to singlet spin conversion occurs between 2 and 1.9\AA above the surface for molecular O_2 and between 1.8 and 1.5\AA for atomic oxygen.

Since an objective of this research is to establish whether dissociated O from the alumina support can diffuse to the catalytic particle and all possible surface diffusion pathways include a bridging conformation, we chose to perform our barrier calculations using a singlet spin state for both the reactant and products. This is the most accurate method to explore the effects of crystal symmetry and surface reconstructions on the dissociation and diffusion barriers for reaction pathways that do not involve a spin change. In future studies, we will perform a detailed sampling of both the triplet and singlet potential energy surfaces using the constrained geometry method to assess the reaction barriers for pathways that involve spin-to-triplet transformations

3. RESULTS AND DISCUSSION

3.1 Effects of Adsorption on Surface Reconstruction

In Table 3, we demonstrate the effect of the adsorption of different species on both the local and long-range reconstruction of the $\alpha\text{Al}_2\text{O}_3$ (0001) surface. Both H and O can directly bind with similar binding energies (~ -30 kcal/mol) to the surface $\text{Al}^{[1]}$ forming a tetrahedron with neighboring $\text{O}^{[2]}$ atoms. By saturating the surface $\text{Al}^{[1]}$, the $\text{O}^{[\text{ads}]}$ reduces the driving force for the contraction of the first inter-atomic layer. Although H binds closer to the surface $\text{Al}^{[1]}$ than O, both H and O produce the same elongation of the local $\text{Al}^{[1]}-\text{O}^{[2]}$ bonding scheme. H and O can also directly bind to the $\text{O}^{[2]}$ atoms. However, in this configuration, there are significant differences in both the adsorption structures

and binding energies ($E_{\text{bind}}^{\text{O}} \sim -50$, $E_{\text{bind}}^{\text{H}} \sim -116$ kcal/mol). Whereas O pulls the $\text{Al}^{[1]} \sim 8\%$ away from the surface, H drives $\text{Al}^{[1]}$ deeper into the lattice. The closer the binding site is to an $\text{Al}^{[1]}$ site, the deeper it is driven into the lattice and the greater the asymmetrical lengthening of the local $\text{Al}^{[1]}-\text{O}^{[2]}$ bonding scheme. This has a profound effect on the relaxation of the top two inter-atomic layers. As the surface $\text{Al}^{[1]}$ is driven into the lattice, it reduces the ability of the oxygen layer to charge compensate for excess charge on the remaining unsaturated surface aluminum atoms, resulting in a

Table 2: Effect of Spin State on O_2 Adsorption Binding Energies and Bond Lengths. The ID notation refers to the structures in Figure 4.

Atomic Oxygen Adsorption				
	E_{binding} (kcal/mol) [Gamallo, 2007]	$\text{O}^{[\text{ads}]}-\text{O}^{[2]}$ (Å)	$\text{O}^{[\text{ads}]}-\text{Al}^{[1]}$ (Å)	\angle_{bond} (degrees)
Triplet A	[-42]	-----	1.782	112
Singlet A	-30 [-35]	-----	1.767	115
Triplet B	[-18]	1.508	1.797	49
Singlet B	-49 [-53]	1.546	1.803	50
Atomic Hydrogen Adsorption				
	E_{binding}	$\text{H}^{[\text{ads}]}-\text{O}^{[2]}$	$\text{H}^{[\text{ads}]}-\text{Al}^{[1]}$	\angle_{bond}
Triplet C	-20	-----	1.626	114
Singlet C	-36	-----	1.625	114
Triplet D	-98	0.971	-----	124
Singlet D	-116	0.972	-----	124
Molecular Oxygen Adsorption / Dissociation				
	E_{binding}	$\text{O}=\text{O}$	$\text{O}^{[\text{ads}]}-\text{Al}^{[1]}$	\angle_{bond}
Triplet E	-7	1.255	1.997	107
Singlet E	-13	1.276	1.959	110
Triplet F	21	1.364	1.895	74
Singlet F	-3	1.393	1.851	76
Triplet G	51	1.499	1.837	48
Singlet G	25	1.522	1.823	49
Molecular Hydrogen Dissociation				
	E_{binding}	$\text{H}^{[\text{ads}]}-\text{O}^{[2]}$	$\text{H}^{[\text{ads}]}-\text{Al}^{[1]}$	\angle_{bond} OH,HOAl
Triplet H	-15	0.982	1.594	110, 120
Singlet H	-14	0.981	1.593	110, 120
Triplet I	-14	0.971	1.621	120, 113
Singlet I	-10	0.972	1.615	121, 112
Triplet J	-85	0.973	-----	127, ---
Singlet J	-67	0.973	-----	127, ---
H_2O Adsorption / Dissociation				
	E_{binding} [Hass, 2000]	$\text{H}^{[\text{ads}]}-\text{O}^{[2]}$	$\text{O}^{[\text{ads}]}-\text{Al}^{[1]}$	\angle_{bond} OH,OAIO
Triplet K	-27 [-23]	0.982	1.982	----, 87
Singlet K	-26 [-23]	0.983	1.987	----, 86
Triplet L	-40 [-33]	0.982	1.740	110, 112
Singlet L	-38 [-33]	0.981	1.740	109, 114
Triplet M	-38 [-33]	0.972	1.759	121, 97
Singlet M	-34 [-33]	0.973	1.758	122, 97

smaller contraction of the first inter-atomic layer.

O₂ and H₂O can molecularly adsorb to surface Al^[1] with binding energies of ~20kcal/mol, whereas H₂ cannot. O₂ adsorbs closer to the surface than H₂O and does not change the contraction of the first inter-atomic layer. In contrast, molecularly adsorbed H₂O causes the surface Al^[1] to contract below the O^[2] atoms, changing the surface termination from Al-terminated to O-terminated although the Al and O atoms are nearly coplanar.

As shown in Figure 4, there are three unique configurations for the dissociated products, henceforth referred to as 1-2, 1-4, and 2-2 dissociation. H₂ can form all three dissociation products. However, H₂O cannot form 2-2 dissociation products and O₂ cannot form 1-4 dissociation products. In comparing the dissociation products, the following trends are clear: (1) dissociation reduces the contraction of the first inter-atomic layer regardless of which species is dissociating and (2) E_{bind} O₂ > E_{bind} H₂ > E_{bind} H₂O. In regards to which type of dissociation product has the lowest energy, it depends on which species are present. For both H₂O and O₂, the lowest energy dissociation products are 1-2. However for H₂, the lowest energy dissociation product is 2-2.

Table3: Effect of Adsorption on Surface Reconstruction. Note: Layer 1 and Layer 2 are the percent change in the 1st and 2nd inter-atomic layers with respect to their bulk coordinates. A negative sign for Layer 1 or 2 represents a contraction of the layer. ΔX^[bind] calculates how much the adsorbate pulls the surface Al^[1] site from its original relaxed position. Al^[1]-O^[2] are the surface bonds neighboring the adsorption site.

	Layer1	Layer2	ΔAl ^[1]	Al ^[1] -O ^[2]		
	(%)	(%)	(%)	Å		
Al ₂ O ₃	-89	+6	-----	1.704	1.704	1.704
O (A)	-83	+6	+11	1.783	1.783	1.783
O (B)	-98	+9	+8	1.826	1.715	1.714
H (C)	-87	+6	+11	1.784	1.784	1.784
H (D)	Non uniform		-14	1.841	1.747	1.746
O ₂ (E)	-90	+7	+7	1.735	1.735	1.733
O ₂ (F)	-84	+4	+9	1.878	1.711	1.710
O ₂ (G)	-86	+13	+13	1.869	1.862	1.733
H ₂ (H)	-83	+10	+13	1.920	1.764	1.764
H ₂ (I)	-84	+9	+11	1.796	1.790	1.770
H ₂ (J)	Non uniform		-16	1.844	1.837	1.745
H ₂ O (K)	-104	+6	+6	1.733	1.721	1.720
H ₂ O (L)	-83	+9	+13	1.894	1.755	1.755
H ₂ O (M)	-85	+7	+11	1.793	1.779	1.766

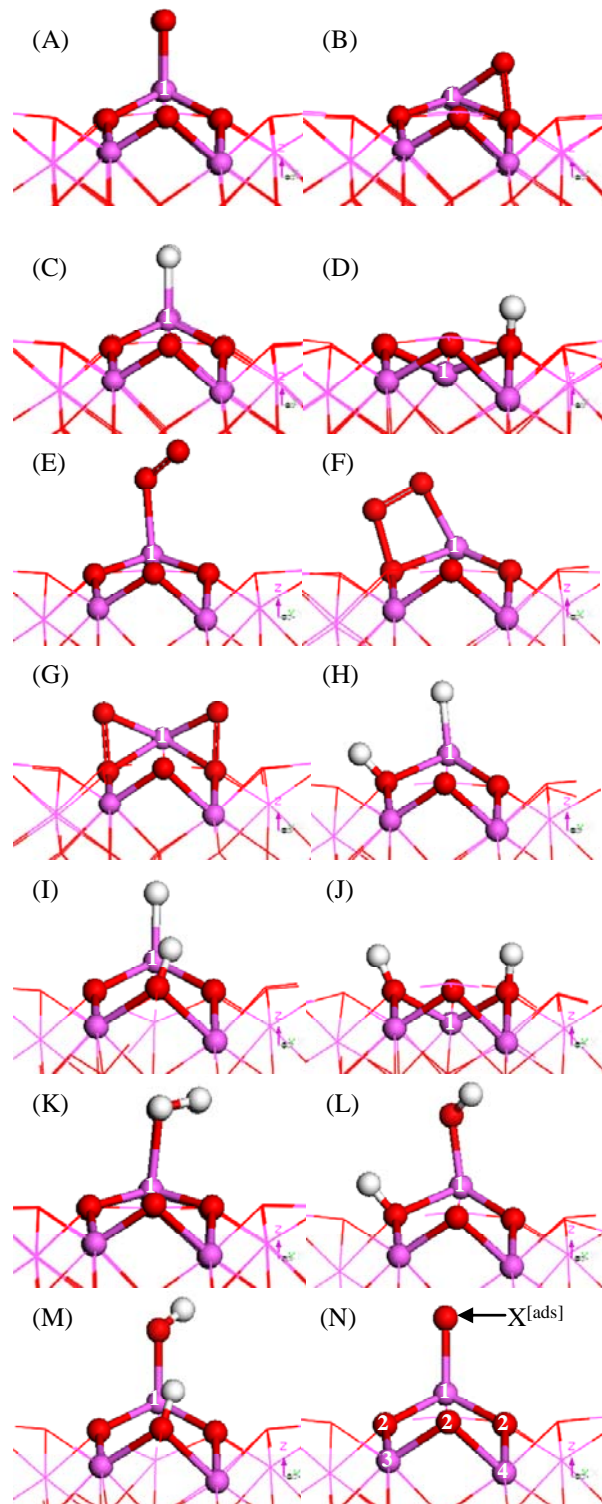


Figure 4: Adsorption and dissociated structures for: (A) Oxygen Tetrahedron (B) Oxygen Bridge (C) Hydrogen Tetrahedron (D) Hydrogen (E) 1-1 Molecularly adsorbed O₂ (F) 1-2 Dissociated O₂ (G) 2-2 Dissociated O₂ (H) 1-2 Dissociated H₂ (I) 1-4 Dissociated H₂ (J) 2-2 Dissociated H₂ (K) 1-1 Molecularly Adsorbed H₂O (L) 1-2 Dissociated H₂O

(M) 1-4 Dissociated H₂O (N) Key indicating atomic layer to which atom originally belonged.

3.1 O₂ Molecular and Dissociative Adsorption

The molecular and 1-2 dissociative adsorption of O₂ from free O₂ appears to be spontaneous. However, the actual barrier for direct and indirect (i.e. from molecularly adsorbed) 1-2 dissociation cannot be determined using the LST transition state method because the reaction involves a triplet-singlet spin conversion which can only be accurately described by sampling both the triplet and singlet potential energy surfaces. However, we can accurately calculate the barriers to the further dissociation of 1-2 into 2-2 products since the minimum energy structure for both of these structures is a singlet spin state. We find that the further dissociation of 1-2 adsorption products is highly endothermic and not kinetically favorable ($E_{\text{rxn}} = 28$ kcal/mol, $E_{\text{barrier}} = 53$ kcal/mol). Given these results, the dissociation of O₂ is not considered a viable source for isolated substrate bound atomic oxygen.

3.2 Water Adsorption and Dissociation

The question arises as to whether dissociated H₂O can serve as a source of substrate bound oxygen. To answer this question, we investigated the following five pathways for the adsorption and dissociation of H₂O:

- (1) free H₂O molecularly (Figure 4K) adsorbs to Al^[1]
- (2) free H₂O dissociates into a 1-2 conformation (Figure 4L) by forming hydroxyls with Al^[1] and its first nearest neighboring O^[2]
- (3) free H₂O dissociates into a 1-4 conformation (Figure 4M) by forming hydroxyls with Al^[1] and its second nearest neighboring O^[2]
- (4) adsorbed H₂O dissociates into a 1-2 conformation
- (5) adsorbed H₂O dissociates into a 1-4 conformation

Our results indicate that water spontaneously dissociates into both 1-2 and 1-4 conformations. Both dissociated products have equivalent adsorption energies. Water can also adsorb molecularly to surface Al with a slightly higher energy than its dissociated product (~+10kcal/mol). The barrier for the molecular adsorption of water is 0.083 kcal/mol which is within the limits of the accuracy of the model. Once molecularly adsorbed, the barrier to further dissociation into 1-2 and 1-4 products are 23 and 9.6 kcal/mol respectively. Experimentally (Elam, 1998), there has been no evidence found for the existence of molecularly adsorbed H₂O. Since the energy released due to spontaneous dissociation from free water is well in excess of the barriers for dissociation from molecular water, our results suggest that if molecular water exists on the surface, it is unlikely to have a long lifetime.

The next series of questions that arise is (1) Can hydrogen diffuse away from dissociated H₂O? and (2) Can the remaining Al^[1]OH hydroxyl group further dissociate into a H and O pair? We find that the easiest paths for the H to diffuse away from dissociated H₂O are paths 10, 13, 15 ($E_{\text{barrier}} \sim 17$ -24 kcal/mol). These paths avoid the influence of Al^[1] and Al^[3] atoms. For all other paths considered, the barrier to the diffusion of H from dissociated H₂O was > 40 kcal/mol. The barrier to the further dissociation of the remaining Al^[1]OH hydroxyl into 2-2 and 2-4 OH dissociation pairs is 45 and 34 kcal/mol, respectively.

3.3 Oxygen Surface Diffusion

The final question to be answered is whether the isolated substrate bound oxygen that is produced from the dissociation of H₂O can diffuse across the Al₂O₃ surface to the catalytic particle to promote combustion. In Table 4, we provide barrier calculations for diffusion of O and H between all allowed surface sites. We find that oxygen can easily diffuse from Al^[1] tetrahedron (Figure 4A) to a bridging (Figure4B) conformation ($E_{\text{barrier}} = 4$ kcal/mol). Once in a bridging conformation, oxygen can diffuse between bridging sites that neighbor the same surface Al^[1] ($E_{\text{barrier}} = 27$ kcal/mol). However, jumping to bridging sites on a different surface Al^[1] atom requires a minimum of 47 kcal/mol. We also calculated the diffusion barrier for a concerted diffusion path in which O^[ads] displaces an O^[2] which moves into a bridging site on the neighboring Al^[1]. The barrier to concerted O diffusion is 61kcal/mol. These results suggest that in the absence of any other species, O becomes localized near

Table4: Surface Diffusion of bound O and H.

Note: O diffusion along paths 1,2,12, 3, 7, 11 involves a triplet-singlet spin change and must be studied in more detail before the diffusion barriers can be verified.

Path ID	Oxygen	Hydrogen	H assisted O
	E_{barrier}	E_{barrier}	E_{barrier}
1	4	18	-----
2	4	18	-----
12	22	99	-----
4	27	42	1
14	27	42	3
16	47	42	3
5	46	34	45
6	47	34	46
9	67	34	43
10	65	18	48
13	64	19	48
15	64	19	46
3	68	34	-----
7	49	25	-----
11	68	107	-----

the surface Al^[1] sites. However, several of the diffusion paths involve singlet to triplet conversion and need to be further studied before this conclusion can be confirmed.

We also studied whether the presence of pre-adsorbed H can promote oxygen diffusion. We find that pre-adsorbed H nearly eliminated the barriers to oxygen diffusion around Al^[1] sites and reduced the barriers along paths 10, 13, and 15 by 17 kcal/mol. However, this improvement was not adequate to allow oxygen to completely transverse a unit cell. Alternatively, when oxygen and hydrogen are allowed to diffuse as a pair, the maximum barrier encountered while traversing the unit cell is 24 kcal/mol. These results suggest that the presence of both mobile O and H species are required for O surface diffusion.

3.4 H₂ Dissociation

H₂ cannot molecularly adsorb to the Al terminated α -Al₂O₃ surface. However, it is both thermodynamically and kinetically favorable for H₂ to dissociate into 1-4 ($E_{\text{barrier}} = 20$ kcal/mol, $E_{\text{rxn}} = -9$ kcal/mol) and 2-2 ($E_{\text{barrier}} = 2$ kcal/mol, $E_{\text{rxn}} = -60$ kcal/mol) dissociation products. These results support the experimental measurements of Wang, 1996 who postulated that hydrogen adsorbed to the Al₂O₃ support resulted in a dramatic increase in the H₂ response during TAP analysis.

3.5 Hydrogen Surface Diffusion

From the results in Table 4, we find that hydrogen can diffuse from a Al^[1] tetrahedron site (Figure 4C) to either the first ($E_{\text{barrier}} = 18$ kcal/mol) or second nearest neighboring oxygen atom ($E_{\text{barrier}} = 26$ kcal/mol). Once in these conformations, diffusion between O^[2] sites neighboring the same surface Al^[1] site is unlikely ($E_{\text{barrier}} = 42$ kcal/mol). However, H can diffuse between O^[2] sites neighboring different Al^[1] sites with barriers of 18 and 34 kcal/mol depending on how close the sub-surface Al atoms are to the diffusion path.

4. CONCLUSIONS

In summary, we provide a theoretical model for reaction processes that occur on the Al₂O₃ substrate and influence combustion at the catalytic particle. Our model suggests that H₂O is a primary source of mobile oxygen and hydrogen species. Once dissociated, H can diffuse away from dissociated water leaving behind an Al^[1]-OH hydroxyl which can also further dissociate creating a 2-2 O-H pair. Although isolated O atoms encounter large barriers to surface diffusion, the 2-2 dissociated O-H pair can diffuse with a barrier ~24 kcal/mol. We also find that H₂ dissociation is an active source of mobile H species. Although O₂ can adsorb molecularly, it cannot

further dissociate to create mobile oxygen. However, given that the presence of pre-adsorbed H had a profound influence on the surface diffusion of O, it may be likely that H can also influence the dissociation of molecularly adsorbed O₂.

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